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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 4 : H01M 8/10 | A1

(11) International Publication Number: WO 86/ 06879

(43) International Publication Date: 20 November 1986 (20.11.86)

(21) International Application Number: PCT/US86/01049

(22) International Filing Date: 15 May 1986 (15.05.86)

(31) Priority Application Number: 734,992

(32) Priority Date: 17 May 1985 (17.05.85)

(33) Priority Country: US

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(81) Designated States: AU, BE (European patent), BR, DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, NL (European patent), SE (European patent).

Published
With international search report.

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(54) Title: PROTON EXCHANGE POLYMER FILM FUEL CELLS

(57) Abstract

An electrochemical cell component having two planarly disposed electrodes bonded to or intimately pressed against opposing sides of a proton exchange active film; said film having: (a) sulfonyl ion exchange active groups present in their protonated form; (b) an equivalent weight of less than about 1000; and (c) a storage modulus of greater than about 1 x 10^8 dynes/square centimeter at a temperature greater than about 110°C. The invention is particularly useful in proton exchange polymer film fuel cells.

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PROTON EXCHANGE POLYMER FILM FUEL CELLS

The present invention relates to fuel cells and particularly to acid electrolyte fuel cells having a proton exchange polymer film.

Fuel cells are electrochemical devices which convert chemical energy directly into electrical energy by the oxidation of a fuel supplied to the cell. A fuel cell is generally composed of two gas diffusion electrodes adjacent to, and in contact with, an electrolyte. The fuel cell includes a means for supplying a fuel to a positive electrode and an oxidant to a negative electrode. Positioned between the electrodes is a solid or liquid electrolyte.

Fuel cell electrolytes transport ionic species between the positive and negative electrodes. Electrolytes may be operable at relatively high temperatures (greater than about 210°C), such as in solid oxide fuel cells, wherein a solid conductive ZrO_2 is the means for ion conduction.

At lower temperatures (less than about 210°C), liquid electrolyte fuel cells of various kinds are well known. These generally are classified as alkaline or

acid electrolyte fuel cells. Alkaline fuel cells use aqueous solutions of sodium or other alkali metal hydroxides as the ion conducting means. Acid fuel cells use acid electrolytes such as sulphuric acid, trifluoromethanesulfonic acid, or phosphoric acid as the ion conducting means.

One type of acid electrolyte fuel cell employs proton exchange polymer films as the electrolyte. There, the electrolyte is the plurality of acid functional groups chemically bonded to the polymer film's polymer backbone. These proton exchange polymer films may be, for example, a sulfonated polystyrene, or more preferably, a substantially fluorinated sulfonic acid polymer such as DuPont's Nafion ion exchange polymer film. The term "solid polymer electrolyte" is often used to describe these ion exchange polymer film structures.

Proton exchange polymer film fuel cells are well known and are described, for example, in U.S. Patent 3,134,697. Early solid polymer electrolyte proton exchange polymer film fuel cells, although operable, experienced limited life because of the chemical instability of the polymer films themselves. However, the subsequent development of perfluorinated ion exchange active polymeric materials such as DuPont Nafion made possible fuel cells of this type with good operating characteristics and lifetimes of many thousands of hours.

Solid polymer electrolyte proton exchange polymer film fuel cells employing Nafion perfluorosulfonic acid polymer films generally operate at temperatures of about 80°C. Because the polymer film itself

is substantially gas impermeable, no porous support matrix is needed in order to prevent gas mixing (as is generally the case with liquid electrolyte fuel cells). With proper external support, pressure differentials of 100 psi, or more, between the fuel gas and the oxidant gas can be realized in actual operation. These characteristics are highly desirable, and make it possible to operate these fuel cells with air as an oxidant by increasing the pressure of the air such that a higher partial pressure of oxygen is attained while not requiring compression of the fuel gas also. Thus, for example, a hydrogen/air fuel cell may operate with one atmosphere pressure on the fuel side while operating at four or more atmospheres pressure of air on the oxidant side of the cell.

In practice, the electrodes are generally physically bonded to the active proton exchange polymer film by a pressure/heat process. See, for example, U.S. Patent 4,272,353.

Although these fuel cells present desirable properties, they are quite expensive because of a combination of polymer film cost and cost of the platinum and other precious metal catalysts required to make successful, long lasting fuel cell electrodes. A way of reducing the cost of power produced in these fuel cells would be highly desirable.

In the present state of the art, the perfluorosulfonic acid polymer films manufactured by DuPont, as described in U.S. Patent 3,282,875, are employed as a film having an equivalent weight of about 1100-1200. Equivalent weight means the weight of polymer which will neutralize one equivalent of base. It is thought

that the ionic conductivity of the polymer film is inversely proportional to the equivalent weight of the polymer film. It is thought that Nafion ion exchange polymer film polymers having lower equivalent weights than those used in the present state of the art may exist (see European Patent Application 0,122,049), however, the physical stability of polymer films having equivalent weights below about 950 are poor, as reported in "Dual Cohesive Energy Densitites of Perfluorosulphonic Acid (Nafion) Membrane", Polymer, Vol. 21, pp. 432-435, April 1980. It would be highly desirable to decrease the equivalent weight of the proton exchange solid polymer electrolyte polymer film in order to reduce the resistance power loss of ion transfer in the fuel cell while at the same time retaining acceptable physical properties.

One way of reducing the ionic resistance of Nafion ion exchange polymer films is by incorporating as much water as possible into the polymer film and increasing the ratio of water contained per ionic functional group. This may be done by saturating the polymer film with water under temperature and pressure conditions more extreme than those normally encountered in use (see U.S. Patent 3,684,747). This treatment has been found necessary to achieve optimum performance of the Nafion polymer film in certain proton-exchange applications (see "Solid Polymer Electrolyte Water Electrolysis", H. Takenake, E. Torikai, Y. Kawami and H. Wakabayashi; Int. J. Hydrogen Energy, Vol. 7, No. 5, pp. 397-403, 1982). Nafion as a proton exchange solid polymer electrolyte polymer film experiences a permanent performance loss when operated for a substantial period of time under drying conditions. As used herein, drying condition means the condition in which the

polymer film or a portion of the polymer film is contacted with fuel gas or oxidant gas which is substantially unsaturated with water at the operating temperatures of the cell for a time sufficient to remove a substantial portion of the water from the polymer film.

When Nafion perfluorosulfonic acid polymer is dry and is in its acid form (having pendant groups that terminate in $-SO_3H$), a softening, or glass-like transition occurs at a temperature of approximately 110°C as determined by the Tan Delta vs. temperature plot, as determined by the DMS experiments discussed later. This transition is known as the alpha transition ("Dynamic Mechanical Studies of Partially Ionized and Neutralized Nafion Polymers", Thein Kyu, Mitsuaki Hasihyama, and A. Eisenberg, Can. J. Chem., Vol. 61, p. 680, 1983).

When drying conditions are experienced in the fuel cell, a rearrangement of ionic regions is thought to occur because of changes in visco-elastic properties of the polymer. ("Intrinsic Conductivity of Perfluorosulfonic Acid Membranes and Its Implication to the Solid Polymer Electrolyte (SPE) Technology", Richard S. Yeo, Proceedings of the Symposium on Transport Processes in Electrochemical Systems, edited by R. S. Yeo, Theodore Katan, Der-Tau Chin, Proceedings Volume 82-10, The Electrochemical Society, Inc., Pennington, N.J. 08534). When a polymer film is dried, the beneficial effect of the water swelling of the Nafion proton exchange polymer film is lost, and the polymer film has a higher ionic resistance. Re-equilibration of the polymer film to its former level of hydration is not easily done in situ in the fuel cell. Drying conditions may also cause physical damage to the polymer film which may

result in cracks or tears in the polymer film. This may allow mixing of the fuel gas and the oxidant and cause catastrophic failure of the cell.

It has been surprisingly found that it is possible, by the practice of the present invention, to decrease the equivalent weight of the solid polymer electrolyte while at the same time limiting the water uptake of the polymer film per functional group, compared to polymer films of the prior art.

Also, contrary to known art, it has been found possible to increase the ionic conductivity of the proton exchange polymer film of the present invention while reducing the water uptake of the solid polymer electrolyte polymer film per functional group.

It is also desirable to achieve the maximum efficiency of conversion of fuel gas available energy to valuable electrical energy, while at the same time also recovering the maximum amount of total electrical and heat energy possible; therefore, it is desirable to operate a fuel cell at temperatures such that a suitable level of steam pressure may be achieved by recovery of the fuel cell waste heat. For practical use as a heat source, pressures of about 15 to about 30 pounds per square inch gauge (psig) are usually sufficient. These steam pressures correspond to temperatures of about 120°C to about 135°C.

It has been surprisingly discovered that the solid polymer electrolyte polymer film prepared according to the present invention have unique physical properties which are seen to be useful in higher temperature proton exchange polymer film fuel cells.

The invention is an electrochemical cell component having two planarly disposed electrodes bonded to or intimately pressed against opposing sides of a proton exchange active film;

said film having:

(a) sulfonyl ion exchange active groups present in their protonated form;

(b) an equivalent weight of less than about 1000; and

(c) a storage modulus of greater than about 1×10^8 dynes/square centimeter at a temperature greater than about 110°C.

The invention is particularly useful in proton exchange polymer film fuel cells.

In describing the present invention, there are a number of physical properties used.

"Dynamic Mechanical Stress" (DMS) is a measure of the visco-elastic response of a polymer found by measuring the stress of the polymer versus the strain exerted on the polymer. DMS measures the storage modulus and the loss modulus, as discussed below. Commercial instruments are available to measure DMS, for example, the Rheometrics Mechanical Spectrometer. Such measurements are well known to those familiar with polymer chemistry.

"Storage modulus" measures the relative stiffness of a material. A drop in the modulus indicates a change in the polymer, such as a transition or a motion. A lower storage modulus indicates the

material is not as stiff as a material having a higher storage modulus. A decrease in the storage modulus occurring over a narrow temperature range, is evidence of a glass-like to rubber-like transition taking place.

"Loss modulus" is a measure of the dissipation of energy (as heat) by friction of the polymer chains in motion as they react to an applied stress.

"Tan Delta" is a calculated value equal to the ratio of the loss modulus to the storage modulus.

The "alpha transition" is the high temperature transition as seen in the Tan Delta vs. temperature plot for the protonated form of this class of perfluoro-sulfonic acid polymer films such as Nafion and those of the present invention. See "Dynamic Mechanical Studies of Partially Ionized and Neutralized Nafion Polymers", Thein Kyu, Mitsuaki Hasihyama, and A. Eisenberg, Can. J. Chem., Vol. 61, p. 680, 1983, for a more complete discussion of the alpha transition.

To be useful in the present invention, the proton exchange active film has (1) sulfonyl ion exchange active groups present in their protonated form, (2) an equivalent weight of less than about 1000, and (3) a storage modulus of greater than 1×10^8 dynes per square centimeter at a temperature greater than about 110°C.

Polymers suitable for use in the present invention contain sulfonic proton exchange groups in their protonated form, i.e. $-SO_3H$. Since most patents teach the preparation of polymer films in their $-SO_2F$ form, the polymer must be converted to its protonated

form. This is generally done by hydrolysis of the $-SO_2F$ form of the polymer film to the metal salt form using a base such as NaOH or KOH. Subsequently, the metal salt form of the polymer film is converted to the protonated form ($-SO_3H$) using an acid such as sulfuric acid or hydrochloric acid. Such conversions are well known to persons knowledgeable in the art and are illustrated in the examples of the present invention.

The polymer films of the present invention have an equivalent weight less than about 1000. In lower temperature fuel cells (less than about 100°C) lower equivalent weight polymer films (about 600 to about 800) seem to be preferable. However, at higher operating temperatures (up to about 150°C) higher equivalent weight polymers (from about 800 to about 1000) may be preferable.

It may generally be said that the lower the equivalent weight, the better for ionic conductivity. However, film properties decrease as the equivalent weight decreases and a compromise between the two must be met. Thus, polymers having equivalent weights below about 500 tend to have such poor film properties, that they are generally not useful in the present invention.

The equivalent weight of the polymer should be as low as possible to reduce resistance power loss in the solid polymer electrolyte means, however the advantageous physical properties of the present invention must preferably be maintained.

In defining the present invention, it is helpful to describe a useful range of polymer properties in the precursor form ($-SO_2F$) by referring to an apparent

viscosity measurement. Polymers found most useful in the scope of the present invention are those having an apparent viscosity in the precursor form of above about 10^3 poise when the shear rate is from about 10/second to about 100/second and at a maximum temperature not to exceed the decomposition temperature of the precursor form of the polymer. This temperature generally is about 300°C but may be from about 250°C to about 350°C. Of course, higher viscosity materials may be employed; however, to be preferably useful it is advantageous that they be fabricable by means such as pressing or extrusion to form precursor polymer film films with acceptable melt strength properties. Notwithstanding, other fabrication methods, such as solution casting may be employed.

It has been discovered that polymers having viscosities below about 1.4×10^3 at shear rates of about 100/ sec. and viscosities below about 2.2×10^3 at shear rates of about 10/sec. were not sufficiently viscous to form suitable films. Conversely, polymers having viscosities greater than about 1.6×10^4 at shear rates of about 100/sec. and viscosities greater than about 7.5×10^4 at shear rates of about 10/sec. were too viscous and were difficult to work with to form films.

It has been found that the most useful polymers have a relatively short pendant chain. These may be copolymers, terpolymers, or homopolymers, providing that they may be made in useful ion exchange capacities according to the method employed.

Suitable polymers and their preparation methods are described, for example, in U.S. Patents 3,282,875; 4,330,654; 4,337,137; 4,337,211; 4,358,412; 4,358,545; 4,417,969; 4,462,877; 4,470,889; and 4,478,695. These polymers, to be useful in the present invention, must be employed in their protonated form.

The polymers that are most preferred for use in the present invention include polymers having at least two monomers, one selected from the first group of monomers and a second selected from a second group of monomers. Optionally, the polymer may include a third monomer selected from a third group of monomers.

The first monomer consists of one or more monomers selected from the group consisting of tetrafluoroethylene, trifluoromonochloroethylene, trifluoroethylene, vinylidene fluoride, 1,1-difluoro-2,2-dichloroethylene, 1,1-difluoro-2-chloroethylene, hexafluoropropylene, 1,1,1,3,3-pentafluoropropylene, octafluoroisobutylene, ethylene, vinyl chloride, trifluoronitrosomethane, perfluoronitrosoethane and alkyl vinyl ester.

The second monomer consists of one or more monomers selected from compounds represented by the general formula:

$$Y\text{-}(CF_2)_a\text{-}(CFR_f)_b\text{-}(CFR'_f)_c\text{-}O\text{-}[CF(CF_2X)\text{-}CF_2\text{-}O]_n\text{-}CF{=}CF_2$$

where
Y is $-SO_3H$;
a is 0-6;
b is 0-6;
c is 0 or 1;
provided a+b+c is not equal to 0;

X is Cl, Br, F or mixtures thereof when n>1;

n is 0 to 6; and

R_f and R'_f are independently selected from the group consisting of F, Cl, perfluoroalkyl radicals having from 1 to about 10 carbon atoms and fluorochloroalkyl radicals having from 1 to about 10 carbon atoms.

The third and optional monomer suitable is one or more monomers selected from the compounds represented by the general formula:

$$Y'-(CF_2)_{a'}-(CFR_f)_{b'}-(CFR'_f)_{c'}-O-[CF(CF_2X')-CF_2-O]_{n'}-CF=CF_2$$

where

Y' is Cl or Br;

a' and b' are independently 0-3;

c' is 0 or 1;

provided a'+b'+c' is not equal to 0;

n' is 0-6;

R_f and R'_f are independently selected from the group consisting of Br, Cl, F, perfluoroalkyl radicals having from 1 to about 10 carbon atoms, and chloroperfluoroalkyl radicals having from about 1 to about 10 carbon atoms;

X' is F, Cl, Br, or mixtures thereof when n'>1.

Also, it is preferable to attain usable physical properties in the proton-active form ($-SO_3H$) of the polymer films of the present invention; so that substantial resistance to tearing or puncturing is attained. These criteria may be described by various tests well known to those skilled in the art, such as Mullin burst strength and elongation at break (tensile) Perhaps one of the better measurements to determine the suitability of polymers for use in the present invention

is the storage modulus. The storage modulus of a polymer may be obtained using instruments designed to measure DMS, as described above and shown in the examples.

The methods employed in manufacturing polymers useful in the present invention are well known to those skilled in the art. For example, polymerization methods may be conducted in an aqueous media using a free radical initiator, see for example, U.S. Patent 3,282,875. However, the polymerization methods must be adjusted according to the specific reactant species, reaction conditions, and process to obtain polymers having equivalent weights less than about 1000.

The polymer films of the present invention may also be used unsupported or used with a porous matrix structure or a supporting scrim. In this manner, physical properties acceptable for some process applications may be realized.

For use in a proton exchange solid polymer electrolyte polymer film fuel cells, the supported polymer films of the present invention may be prepared and supported to be capable of withstanding pressure differentials of over about 100 psi. It is preferred that a proton exchange electrolyte polymer film of the present invention be capable of maintaining separation of fuel and oxidant gases wherein the pressure differential employed is at least about 15 psi.

The present invention is particularly suitable for use in a fuel cell. Fuel cells of the type having a proton exchange polymer film used in a solid polymer electrolyte form are particularly suitable. Such cells

are well known in the art and are described, for example, in Fuel Cells and Fuel Batteries, H. A. Liebhafsky and E. J. Cairus, John Wiley and Sons, New York, 1968.

One type of fuel cell suitable for use with the present invention comprises a container holding the components of the fuel cell. The size and shape of the container is not critical. However, the walls of the container should be of sufficient thickness, integrity and strength to hold the contents of the fuel cell. The materials of construction contacting the internal components of the fuel cell are preferably substantially completely unreactive with the internal components of the cell. Suitable materials of construction include such things as niobium, titanium, Kynar (a registered trademark of Pennwalt Corporation) and graphite.

The cell has at least two electrodes, an anode and a cathode. A variety of materials are suitable for use as electrode catalysts including such things as platinum group metals and platinum black. The electrodes are bonded to or in intimate contact with the polymer film. Methods for making suitable electrodes are defined in U.S. 4,272,353.

Positioned between and in contact with each of the electrodes is a solid polymer electrolyte material. The solid polymer electrolyte material is an ion exchange active polymer which has sulfonyl ion exchange active groups.

For proper operation of the fuel cell of the present invention, it is preferable for the solid polymer electrolyte film to be substantially impermeable to the reactant gases. The gas permeability of the

proton exchange polymer film seems to be related to the water content of the polymer film. A polymer film having good film properties may have high gas permeability, or a polymer film having poor film properties may have low gas permeability. It is desirable to have as low a gas permeability as possible while retaining sufficient mechanical strength.

The anode and the cathode should both be in intimate contact with the solid polymer electrolyte. Such contact can be assured by bonding the electrodes to the solid polymer electrolyte, or by pressing the electrodes against the solid polymer electrolyte. In a solid polymer electrolytic cell, the stack is generally loaded hydraulically by means of a bladder or by mechanical compression to maintain the electrical contact of the components, see, for example; "Interim Report New Membrane Catalyst for Solid Polymer Electrolyte Systems", P.O. No. 9-X53-D6272-1 Project Engineer, R. J. Lawrence, prepared for University of California, Los Alamos National Lab, Los Alamos, N.M. 87545.

The polymer film is preferably pre-conditioned by contacting the polymer film with water at about the temperature at which the polymer film will be kept in an operating electrochemical cell. This has the effect of pre-conditioning the polymer film at about the activity of electrolyte present in the particular electrochemical cell so that it will be substantially dimensionally stable in the cell. It is also preferable to pre-condition the polymer film at such a temperature that no glass transition occurs, so that over-swelling of the ionic regions of the polymer film is avoided. In this manner, irreversible loss of performance upon encountering drying conditions in a fuel cell are thus

prevented. It is preferable in the practice of the present invention to both pre-condition and operate the fuel cell below the alpha transition temperature of the protonated form of the polymer, such that dehydration and re-hydration of the polymer film in a fuel cell are substantially completely reversible.

Polymer films of the present invention may be equilibrated in water under pressure so that they may retain an equilibrium amount of water while operating at temperatures sufficient to produce a useable pressure of steam from waste heat produced in the fuel cell. This may be accomplished while not concurrently surpassing the alpha transition of the polymer. Thus, the water equilibria for these polymer films is thought to be substantially completely reversible at surprisingly high temperatures, resulting in a stable fuel cell which is capable of operating at a higher recovery of useable electrical plus heat energy per unit of fuel energy consumed in the process.

The fuel cells of the present invention may be operated at temperatures above the alpha transition temperature of the polymer film. However, at such temperatures, support of the polymer film may be necessary because the polymer softens. Preferably, therefore, the fuel cells are operated at temperatures less than the alpha transition of the polymer film. For the preferred polymers of the present invention, temperatures less than about 130°C or less than about 110°C are suitable.

The fuel cell of the present invention may be used to produce electrical energy by feeding a fuel to the anode compartment and an oxygen-containing gas to

the cathode. The fuel must contain hydrogen. The hydrogen can be pure hydrogen or it can be mixed with inert gases, such as carbon dioxide. Preferably, the hydrogen gas is as pure as possible. The fuel can be reformed natural gas or other reformed hydrocarbons so long as the carbon monoxide level is kept sufficiently low to avoid poisoning the catalyst present on the electrodes of the fuel cell. The oxidant can be pure oxygen or air. Also, the oxidant can be bromine, chlorine or other oxidants in the case of hydrogen-halide type fuel cells.

The present invention may be used in a variety of other types of electrochemical cells, in addition to fuel cells, including dialysis and electrodialysis cells in which protons are transferred through an electrolyte to adjoining electrodes.

In addition, the present invention may be used in hydrogen-halide cells, such as cells forming HCl or HBr from hydrogen and chlorine or bromine, respectively. The present invention is also suitable for use in water electrolysis cells.

EXAMPLE 1.

This example shows that films can be made that have equivalent weights less than 1000 that have sufficient film properties to allow them to be formed into films.

A series of polymers prepared according to the teaching of U.S. Patent 4,330,654 were analyzed to determine their equivalent weight. The polymers and their equivalent weights are shown below in Table I.

TABLE I

Polymer	Eq. Wt.
"A"	639
"B"	686
"D"	850
"E"	950

The viscosity of each of the polymers was determined at 300°C using an Instron extrusion capillary rheometer. An extrusion capillary rheometer is a miniature ram extruder fitted with a capillary die and instrumented so that melt temperature and pressure behind the die can be monitored. Speed of extrusion can be varied so that the properties of a plastics melt can be determined under a wide range of shear rates. Dies with different lengths and angles of entry are available to permit study of the effect of die design on output and quality of extrudate.

The results are shown in Figure 1. Figure 1 is graphed on a log-log graph. The results show that polymers having equivalent weights less than 1000 have physical properties that make them suitable for forming into films.

Polymers "A" and "B" were formed into films by individually hot pressing each polymer at a temperature of about 300°C. Polymers "D" and "E" were melt extruded.

The films were then converted from their sulfonyl fluoride form ($-SO_2F$) to their sodium salt form ($-SO_3^-Na^+$) by hydrolyzing in a 25 weight % aqueous sodium hydroxide solution at about 90°C for about 8 hours.

Then each of the films was acidified in a 24 weight percent aqueous sulfuric acid solution at about 90°C for about 24 hours. The sample was then washed three times with water. Then, each of the films was hydrated by boiling in water for about two hours. Each was then removed and placed in a sealed plastic bag to prevent drying.

The films prepared from polymer "D" and the films prepared from polymer "E", along with the Nafion polymer film prepared in Comparative Example 2 were tested for tensile strength at break and the degree of elongation at break.

Tensile tests were conducted using an Instron (Model 1125) tensilometer at both room temperature and high temperature/high humidity conditions. A Thermotron environmental chamber, was used to control the temperature at 90°C and the humditiy at 100% for the high temperature test.

Each polymer sample was cut to approximately 3 inches in length and 0.5 inches in width. Using the Instron tensilometer, stress was applied by stretching the polymer film at a rate of 2 inches per minute.

Each polymer was tested at 25°C and 90°C. The films tested at 25°C were tested at ambient atmospheric conditions. To avoid drying, each of the samples were tested immediately after their removal from the sealed plastic bag.

The results of the tests are shown in Table II.

TABLE II

Polymer Film	Eq. Wt.	Temp. (°C)	Stress (psi)	% Elongation at break
"D"	850	25	4200	140
"E"	950	25	3870	150
"D"	850	90	2300	200
"E"	950	90	2700	260

When compared with Nafion polymer film data of Comparative Example 2, this shows that at 25°C polymers D and E were stronger than Nafion, even though polymers D and E had equivalent weights substantially lower than 1000. The results of the samples run at 90°C shows that polymers D and E were stronger and had substantially less elongation.

The films prepared from polymers "A" and "E" were evaluated using Dynamic Mechanical Spectroscopy. The storage modulus and the loss modulus were determined using Dynamic Mechanical Stress techniques. Tan Delta was calculated using the storage modulus and the loss modulus for each of the polymer films over the temperature range of from 15°C to 240°C.

The original dimensions of each of the samples was approximately 60 millimeters (mm) x 12 mm x 3 mm. The polymers were kept in a nitrogen environment throughout the testing. The spectra were recorded with a Rheometrics Mechanical Spectrometer Model 605. The oscillatory frequency of the polymer was 1 Hertz with a 0.2% strain. The samples were removed from their

sealed plastic bag and placed in the DMS unit wet. There, they were individually heated in increments of 5°C and data was taken at each 5° increment.

The results of the tests are shown in Figure 2 as the storage modulus and Figure 3 as Tan Delta. These graphs are made on semi-log paper with the "y" axes being in log form.

It is surprising that polymer films from both Polymer A (639 equivalent weight) and Polymer E (950 equivalent weight) retain a relatively stable visco-elastic condition much past the temperature at which Nafion polymer films begin an abrupt change to a more liquid state, as shown in Comparative Example 3.

Even more surprising, and completely unexpected, is the high value of the alpha transition peaks (glass transition temperatures) exhibited by these films. This shows that these films may be used in fuel cells operated at temperatures above 90°C and even above 100°C to produce steam as a by-product.

Polymer "B" was tested in the same manner. The results of that test is shown in Figure 4. This plot was made on semi-log paper, with the "y" axis being in log form.

Ion exchange films "A", "B", "D" and "E" were individually evaluated to determine the amount of water absorbed by each film using the following procedure:

(1) The film was vacuum dried in its $-SO_3H$ form for about 3 days at about 80°C;
(2) each sample was weighed;

(3) the sample was placed in boiling water for 30 minutes;

(4) each sample was removed from the boiling water and its surface was blotted dry with a towel; and

(5) the film was reweighed to determine how much water had been absorbed.

Steps 2 through 5 were repeated until no further weight change was noted. The difference in weight represented the amount of water absorbed by the film.

The results of the water absorption are shown in Table III and in Figure 5.

TABLE III

(Moles water/equivalent of SO_3H+)

Eq. Wt.	U.S. 4,330,654 Polymers
1625	9.60*
1200	14.2*
1000	17.3*
950 ("E")	18.4
900	19.4*
850 ("D")	18.4
686 ("B")	19.9
639 ("A")	56.8
597	179

*calculated from U.S. Patent 4,358,545

When compared to the data of Comparative Example 4, this data shows that the hydration per functional group in Polymers "A", "B", "D" and "E" is less than the hydration per functional group in polymer films of the prior art. Polymers having a low hydration would be expected to have a lower ionic conductivity than polymers containing more water per functional group. Surprisingly, the ratio of water per functional group in the polymer films of the present invention remains substantially constant from an equivalent weight of from about 1000 to less than about 700. By contrast it is seen that the ratio of water per functional group in the Nafion polymer films of the present state of the art increases significantly with decreased equivalent weight and, it is believed, are not useful below about 1000 equivalent weight because of over swelling.

Ionic conductivity measurements were carried out using a YSI Model 31 Conductivity Bridge using 1000 Hertz.

Films prepared from polymers "A", "B", "D" and "E" were tested for ionic conductivity.

Each of the films was allowed to equilibrate in 5.5 weight percent HCl for 3 days prior to measuring the ionic conductivity.

The film being tested supported the two chambers of the ionic conductivity cell in which there is a platinum black coated platinum electrode in each half.

The results of the ionic conductivity measurements are shown in Figure 6.

When compared to the data of Comparative Example 5, this illustrates that polymer films of the present invention display higher ionic conductivities than those of the state of the art while concurrently retaining less water per unit functional group. Therefore, power loss in a fuel cell is expected to be significantly decreased.

In preparation for its use in a fuel cell, film "E" was soaked in a 25 weight percent caustic solution for about 16 hours at about 80°C to convert the sulfonyl fluoride functional groups to the salt form (Na+). It was removed, washed with boiling water, and dried. A platinum black cathode catalyst was applied to one side of the polymer film and a mixture of noble metals were applied to the other side as an anode catalyst. To apply the catalyst particles, the film was abraded with 600 grit sandpaper. Then an aqueous mixture of catalyst and polytetrafluoroethylene, in an 85:15 weight ratio, was applied to the surface of the polymer film by painting with a fine paint brush. The coated polymer film was then placed in a press held at about 150°C for about 5 minutes. The press pressure was increased to about 1500 pounds per square inch on the coated area of the polymer film. The pressure and the temperature were kept constant for one minute and then reduced to ambient conditions. The catalyst loading was about 4 milligrams catalyst per square centimeter of polymer film and covered an area of about 50 square centimeters.

The coated polymer film was then placed into a 24 weight percent sulfuric acid solution for about three hours at about 90°C to convert the sulfonyl groups to the acid (SO_3H) form. Then, the coated polymer film was washed in water and placed into boiling water for 30 minutes prior to being placed into the fuel cell.

The polymer film was positioned between two pieces of highly porous graphite paper which had been coated with a wetproofing agent (T-30 polytetrafluoroethylene resin sold by E. I. DuPont de Nemours, Inc.). The wetproofed polymer film was sandwiched between two titanium screens. The screens also acted as gas distributing means in the operating fuel cell. The combination was then sandwiched between two pieces of nickel mesh and then fitted between two flanges. The fuel cell was connected to an external load. Each flange had a gas inlet and a gas outlet.

Hydrogen gas was fed through a gas inlet connected to the anode side of the polymer film and oxygen was fed through the gas inlet connected to the cathode side of the polymer film. The open circuit voltage was found to be about 1.2 volts. Upon increasing the load resistance of the cell, the voltage decreased and the voltage at a predetermined current density was recorded. The wattage output of the cell was found to be about 5.15 watts at 188 amps per square foot.

EXAMPLE 2

In preparation for its use in a fuel cell, film "A" was soaked in a 25 weight percent caustic solution for about 16 hours at about 80°C to convert

the sulfonyl fluoride pendant groups to the salt form (Na+). The polymer film was removed, washed with boiling water and dried. A platinum black cathode catalyst was applied to one side of the polymer film and a mixture of noble metals were applied to the other side as an anode catalyst. To apply the catalyst particles, the film was abraded with 600 grit sandpaper. Then an aqueous mixture of catalyst and polytetrafluoroethylene, in an 85:15 weight ratio, was applied to the surface of the polymer film by painting with a fine paint brush. The coated polymer film was then placed in a press held at about 150°C for about 5 minutes. The press pressure was increased to about 1500 pounds per square inch on the coated area of the polymer film. The pressure and the temperature were kept constant for one minute and then reduced to ambient conditions. The catalyst loading was about 4 milligrams catalyst per square centimeter of polymer film and covered an area of about 50 square centimeters.

The coated polymer film was then placed into a 24 weight percent sulfuric acid solution for about three hours at about 90°C to convert the sulfonyl groups to the acid ($-SO_3H$) form. Then, the coated polymer film was washed in water and placed into boiling water for 30 minutes prior to being placed into the fuel cell.

The polymer film was positioned between the two pieces of highly porous graphite paper which had been coated with a wetproofing agent (T-30 polytetrafluoroethylene resin sold by E.I. DuPont). The wetproofed polymer film was sandwiched between two pieces of titanium screen. The screen also acted as a gas distributing means in the operating fuel cell. The

combination was then sandwiched between two pieces of nickel mesh and then fitted between two flanges. The fuel cell was connected to an external load. Each flange had a gas inlet and a gas outlet.

Hydrogen gas was fed through a gas inlet connected to the anode side of the polymer film and oxygen was fed through the gas inlet connected to the cathode side of the polymer film. The open circuit voltage was found to be about 1.2 volts. Upon increasing the load resistance of the cell, the voltage decreased and the voltage at a predetermined current density was recorded. The wattage output of the cell was found to be about 4.6 watts at 188 amps per square foot.

COMPARATIVE EXAMPLE 1

This example shows that some polymer films may have the proper equivalent weight but do not have sufficient strength to be suitable for use in the present invention.

A polymer was prepared according to the teaching of U.S. Patent 4,330,654 and analyzed to determine its equivalent weight. It was found to be 694.

The viscosity of the polymer was determined at 300°C using an Instron extrusion capillary rheometer as shown in Example 1. The result is shown in Figure 1, labeled "C".

Polymer "C" was formed into a film by hot pressing the polymer at a temperature of about 300°C.

The film was then converted from its sulfonyl fluoride form ($-SO_2F$) to its salt form ($-SO_3^-Na^+$) by hydrolyzing in a 25 weight % aqueous sodium hydroxide solution at about 90°C for about 8 hours.

Then the film was acidified in a 20 weight percent aqueous sulfuric acid solution at about 90°C for about 24 hours. The sample was then washed three times with water. Then, the film was hydrated by boiling in water for about two hours. It was then removed and placed in a sealed plastic bag to prevent drying.

The storage modulus of Polymer "C" was tested in the same manner as the polymers in Example 1. The results are shown in Figure 4 labeled "C".

This shows that, although Polymer "C" has sulfonyl exchange groups and has an equivalent weight less than 1000, it does not have a storage modulus within the desired range to make it suitable for use in the present invention.

COMPARATIVE EXAMPLE 2

A commercial Nafion polymer film having an equivalent weight of about 1100 was obtained from E. I. DuPont Company. It was obtained in its potassium salt form under the designation Nafion 117. It was tested for tensile strength at break and the degree of elongation at break in the same manner described in Example 1.

The results of the tests are shown in Table IV.

TABLE IV

Polymer Film	Eq. Wt.	Temp. (°C)	Stress (psi)	% Elongation at break
Nafion	1100	25	2550	140
Nafion	1100	90	1700	>400*

*did not break during test as performed

When compared to the data described in Example 1, this shows that at 25°C Polymers "D" and "E" were stronger than Nafion, even though Polymers "D" and "E" had equivalent weights substantially lower than 1000. The results of the samples run at 90°C shows that Polymers "D" and "E" were stronger and had substantially less elongation.

COMPARATIVE EXAMPLE 3

Literature values of the storage modulus and Tan Delta for a 1200 equivalent weight Nafion polymer film were also plotted in Figures 2 and 3, as curve N, for comparison. See "Dynamic Mechanical Studies of Partially Ionized and Neutralized Nafion Polymers", Thein Kyu, Mitsuaki Hasihyama, and A. Eisenberg, Can. J. Chem., Vol. 61, p. 680, 1983.

COMPARATIVE EXAMPLE 4

The water of hydration was determined for Nafion polymers having various equivalent weights from U.S. Patent 4,358,545. The results are shown in Table V.

TABLE V

(Moles water/equivalent of SO_3H+)

Eq. Wt.	Nafion Polymers
1625	13.8
1200	20
1000	26
950	28.4
900	31
850	35.3

When compared to the data of Example 1, this data shows that the hydration per functional group in Polymers "A", "B", "D" and "E" is less than the hydration per functional group in polymer films of the prior art. Polymers having a low hydration would be expected to have a lower ionic conductivity than polymers containing more water per functional group. Surprisingly, the ratio of water per functional group in the membranes of the present invention remain substantially constant from an equivalent weight of from about 1000 to less than about 700. By contrast it is seen that the ratio of water per functional group in the Nafion polymer films of the present state-of-the-art increases significantly with decreased equivalent weight and, it is believed, are not useful below about 1000 equivalent weight because of over-swelling.

COMPARATIVE EXAMPLE 5

A Nafion ion exchange polymer film having an equivalent weight of 1200 was tested for ionic conductivity as in Example 1, by R. S. Yeo, et al as reported in Transport Processes in Electrochemical Systems, R. S.

Yeo, T. Katan, D. T. Chin, Proceedings, Volume 82-10, The Electrochemical Society, Pennington, N.J. 08534. It showed an ionic conductivity of about 0.058 ohm-1 cm-1. This is shown in Figure 6 as point "N".

When compared to the data of Example 1, this illustrates that polymer films of the present invention display higher ionic conductivities than those of the prior art while concurrently retaining less water per functional group. Therefore, power loss in a fuel cell is expected to be significantly decreased.

I CLAIM:

1. An electrochemical cell component having two planarly disposed electrodes bonded to or intimately pressed against opposing sides of a proton exchange active film;

said film having:

(a) sulfonyl ion exchange active groups present in their protonated form;

(b) an equivalent weight of less than about 1000; and

(c) a storage modulus of greater than about 1×10^8 dynes/square centimeter at a temperature greater than about 110°C.

2. The electrochemical cell component of Claim 1 wherein the film has an equivalent weight less than about 950.

3. The electrochemical cell component of Claim 1 wherein the film has an equivalent weight less than about 900.

4. The electrochemical cell component of Claim 1 wherein the film has an equivalent weight between about 500 and about 1000.

5. The electrochemical cell component of Claim 1 wherein the film has a storage modulus of greater than about 1 x 10^8 dynes/square centimeter at a temperature greater than about 130°C.

6. The electrochemical cell component of Claim 1 wherein the film is a copolymer of at least two monomers,

wherein one monomer is selected from a first group of monomers consisting of tetrafluoroethylene, trifluoromonochloroethylene, trifluoroethylene, vinylidene fluoride, 1,1-difluoro-2,2-dichloroethylene, 1,1-difluoro-2-chloroethylene, hexafluoropropylene, 1,1,1,3,3-pentafluoropropylene, octafluoroisobutylene, ethylene, vinyl chloride, trifluoronitrosomethane, perfluoronitrosoethane and alkyl vinyl ester; and

wherein a second monomer is selected from a second group of monomers consisting of compounds represented by the general formula:

$$Y\text{-}(CF_2)_a\text{-}(CFR_f)_b\text{-}(CFR'_f)_c\text{-}O\text{-}[CF(CF_2X)\text{-}CF_2\text{-}O]_n\text{-}CF{=}CF_2$$

where

Y is $-SO_3H$;

a is 0-6;

b is 0-6;

c is 0 or 1;

provided a+b+c is not equal to 0;

X is Cl, Br, F or mixtures thereof when n>1;

n is 0 to 6; and

R_f and R'_f are independently selected from the group consisting of F, Cl, perfluoroalkyl radicals having from 1 to about 10 carbon atoms and fluorochloroalkyl radicals having from 1 to about 10 carbon atoms.

7. The electrochemical cell component of Claim 1 wherein the film is a copolymer of at least three monomers,

wherein one monomer is selected from a first group of monomers consisting of tetrafluoroethylene, trifluoromonochloroethylene, trifluoroethylene, vinylidene fluoride, 1,1-difluoro-2,2-dichloroethylene, 1,1-difluoro-2-chloroethylene, hexafluoropropylene, 1,1,1,3,3-pentafluoropropylene, octafluoroisobutylene, ethylene, vinyl chloride, trifluoronitrosomethane, perfluoronitrosoethane and alkyl vinyl ester; and

wherein a second monomer is selected from a second group of monomers consisting of compounds represented by the general formula:

$$Y\text{-}(CF_2)_a\text{-}(CFR_f)_b\text{-}(CFR'_f)_c\text{-}O\text{-}[CF(CF_2X)\text{-}CF_2\text{-}O]_n\text{-}CF{=}CF_2$$

where

Y is $-SO_3H$;

a is 0-6;

b is 0-6;

c is 0 or 1;

provided a+b+c is not equal to 0;

X is Cl, Br, F or mixtures thereof when n>1;

n is 0 to 6; and

R_f and R'_f are independently selected from the group consisting of F, Cl, perfluoroalkyl radicals having from 1 to about 10 carbon atoms and fluorochloroalkyl radicals having from 1 to about 10 carbon atoms; and

wherein a third monomer is selected from a third group of monomers represented by the general formula:

$$Y'\text{-}(CF_2)_{a'}\text{-}(CFR_f)_{b'}\text{-}(CFR'_f)_{c'}\text{-}O\text{-}[CF(CF_2X')\text{-}CF_2\text{-}O]_{n'}\text{-}CF{=}CF_2$$

where

Y' is Cl or Br;

a' and b' are independently 0-3;

c' is 0 or 1;

provided a'+b'+c' is not equal to 0;

n' is 0-6;

R_f and R'_f are independently selected from the group consisting of Br, Cl, F, perfluoroalkyl radicals having from 1 to about 10 carbon atoms, and chloroperfluoroalkyl radicals having from 1 to about 10 carbon atoms;

X' is F, Cl, Br, or mixtures thereof when n'>1.

8. The electrochemical cell component of Claim 1 wherein the film has a viscosity above about 1.4×10^3 poise at a shear rate of about 100/sec. and a viscosity above about 2.2×10^3 at a shear rate of about 10/sec. at a temperature of at least about 300°F while the film is in its $-SO_2F$ form.

9. The electrochemical cell component of Claim 1 wherein the film has a viscosity less than about 1.6×10^4 poise at a shear rate of about 100/sec. and a viscosity less than about 7.5×10^4 at a shear rate of about 10/sec. at a temperature of at least about 300°F while the film is in its $-SO_2F$ form.

10. The electrochemical cell component of Claim 1 including a porous support supporting said film.

11. The electrochemical cell component of Claim 10 wherein the supported film has sufficient strength to withstand a pressure differential on its sides of at least about 100 pounds per square inch.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US86/01049

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL. [4] H01M 8/10
US. CL. 429/13

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	204/98, 282, 296 429/13, 33 427/115

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
Y	US, A, 4,272,353, (Lawrance et al), 09 June 1981, See col. 2, lines 26-59, col. 4, lines 46-57 and col. 9, lines 43-65	1-27
Y	US, A, 4,330,654, (Ezzell et al), 18 May 1982 See col. 3, lines 56-68 and col. 4, lines 1-45	1-27
Y	US, A, 4,358,545, (Ezzell et al), 09 November 1982, See col. 6, lines 66-68 and col. 7, lines 1-24	1-27
A	US, A, 3,528,852, (Hodgdon et al), 15 September 1970	
A	US, A, 4,246,090, (Nora et al), 20 January 1981	
A	US, A, 4,462,877, (Ezzell), 31 July 1984	

* Special categories of cited documents: [15]

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [3]	Date of Mailing of this International Search Report [3]
23 June 1986	26 JUN 1986
International Searching Authority [1]	Signature of Authorized Officer [20]
ISA/US	D.L. Walton

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